NANO VISION
An International Open Free Access, Peer Reviewed Research Journal
www.nano-journal.org

ISSN 2231-2579 (Print)
ISSN 2319-7633 (Online)
Abbr: Nano Vision.
2014, Vol.4(1): Pg.13- 16

Stock Shift and Thermal Characteristics of Semiconductor Nanoparticles

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(Received on: February 14, 2014)

ABSTRACT

This paper review recent advances in luminescence of semiconductor nanoparticles. With reducing size of the semiconductor nanoparticles the onset of absorption takes place at longer wavelength.Such blueshift with reducing size of the nanocrystals is the reflection of bandgap increase owind to the quantum confinement effect. In most case blueshift in the peak of the photoluminescence (PL) spectra is observed with reducing size of the nanocrystals, but the luminescence from certain surfsce state may give rise to the redshift with reducing size of the nanocrystals. Whereas the decay time of luminescence decreases, the quantum efficiency of luminescence and Stock shift increase with reducing size of nanoparticles. The PL intensity of nanoparticles decreases with the increasing temperature. It is optimum for a particular concentration of the dopants in the nanoparticles. The luminescence of semiconductor nanoparticles is exciting to the researchers and it has several important potentials.

Keywords: Semiconductor nanoparticles, Photoluminescence and optical properties.

1. INTRODUCTION

Nanoparticle or an ultrafine particle is a small solid whose physical dimension lies in the approximate range of a few nm to a few hundred nm. Semiconductor nanoparticles having size less than the critical size M of charge carriers are called quantum dots or q particles. Nanophase materials generally include nanocrystalline

thin films, sintered materials with ultra fine grain structure, and loosely aggregate nanoparticles.

Size reduction affects most of the physical properties (structural, magnetic, optical, dielectric, thermal, etc.) due to surface effects and quantum size effects. Owing to the extremely small dimensions, these materials exhibit properties, which are fundamentally different from, and often superior to those of their conventional counterpart. In recent past, there has been considerable interest in the study of size effect in semiconductors of reduced dimension (in nanometer scale) due to their applications in optoelectronic devices, single electron devices, resonant tunneling devices, memory devices, magnetic sensors, catalysis, etc.[1-3] Optical spectroscopy being the non-contact method, has proved to be the most suitable technique to monitor the size-evolution of the electronic structure. The present paper reports the thermal and stokes shift characteristics of semiconductor nanoparticles.

2 THEORY

2.1 Thermal characteristic

Fig.(1) shows the effect of thermal characteristic of the quantum efficiency of various size of a Si:H spheres. Greater spatial confinement result in reduced temperature dependence[1,2] have reported a phenomenological model (SJ model) for phosphors and nanocrystalline silicon, which is successful in explaning the temperature dependence of luminescence intensity.

The time integrated PL intensity I(T) in typically written as

$$I(T) = I_o R_r \tau \tag{1}$$

Where the life time τ is given by the competition between the rediative rate R_t and the hopping rate R_{hop} of the carriers

$$\frac{1}{\tau} = R_r + R_{hop} \tag{2}$$

Singh and John[3] have shows that the raditive rate R_r has a week dependence, while the R_{hop} hopping rate has a Birthelot type behavior

$$R_r = \nu_r \exp[-\frac{T_r}{T}] \tag{3}$$

$$R_{hop} = \nu_{hop} \exp[\frac{T}{T_B}] \tag{4}$$

Where ν_r and ν_{hop} are the characteristic frequencies while T_r and T_B are the temperature which are characteristics of the sample. T_B is called the Birthelot temperature of the sample.

From eqs (1) to (4) the temperature dependence of the integrated PL intencity may be expressed as

$$I(T) = \frac{I_o}{1 + (\frac{R_{hop}}{R_r})}$$

or

$$I(T) = \frac{I_o}{1 + (\frac{R_{hop}}{R_r}) \exp\left(\frac{T}{T_B}\right) \exp\left(\frac{T_r}{T}\right)} \tag{5}$$

As $\exp\left(\frac{T_r}{T}\right)$ depends weakly on temperature eq. (5) indicates the decrease of I_T with increasing temperature of the samples.

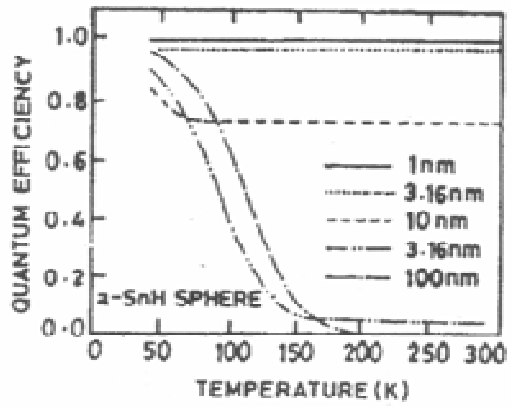

Fig 1- Temperature dependence of the radiative quantum efficiency of a Si: H spheres of diameters from1-100 nm

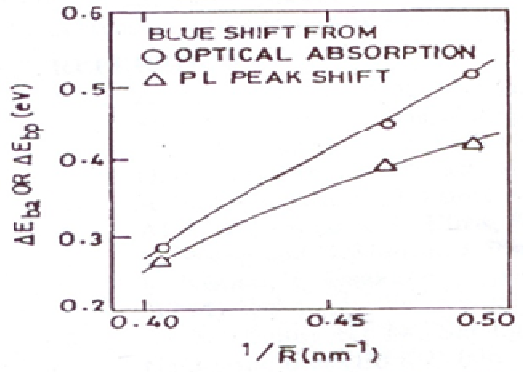

Fig 2 –Dependence of blue shift obtained from the optical absorption and the PL peak shift on the $\left(\frac{1}{R}\right)$, where R is the average grain radias in nm

2.2 Stokes Shift Characteristic

Fig (2) shows that the Stokes shift of ZnTe nanocrystals increases with reducing size of nanocrystals[4]. Similer effect has been observed for ZnS:Mn and CdS nanocrystals.

It is known that the number of phonons emitted just after the absorption transition in the configuration coordinates of q = 0 is given by:

$$S = \frac{M_a \Omega q_o^{\,2}}{2h} \qquad (6)$$

where M_a = mass of the atom, Ω = vibrational frequency, q_0 = the configuration coordinate corresponding to the minimum energy of the excited state and h = Planck's contant.

The increase of Stokes shift with reducing size of the nanocrystals Is not satisfactorily understood totodate. It seems that increasing value of both Ω and q_0 may be responsible for this fact.

3. CONCLUSIONS

The important conclusions are drawn from the present investigation:

(i) The PL intensity is optimum for a particular dopant concentration in the nanocrystals.
(ii) The PL intensity decreases with decreasing size of the nanoparticles.
(iii) It is found that the stokes shift increase with the decreasing size of nanoparticles.

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